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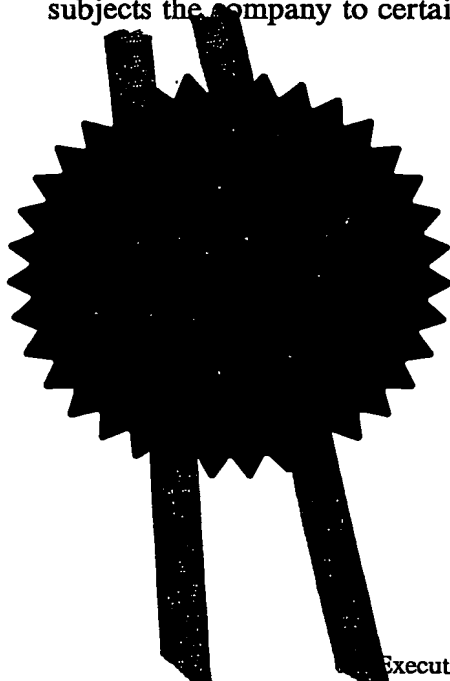
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0223817.8

150CT02 E755601-1 D02944

P01/7700 0.00-0223817.8

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Avecia Limited
Hexagon House
Blackley
Manchester, M9 8ZS
United Kingdom

12 OCT 2002

Patents ADP number (if you know it)

07764137001 ✓

If the applicant is a corporate body, give the country/state of its incorporation

GB

4. Title of the invention

Compounds, Compositions and Uses

5. Name of your agent (if you have one)

MAYALL, John

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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United Kingdom

Patents ADP number (if you know it)

6244313002

7764137001

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Number of earlier application

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Claim(s)

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Abstract

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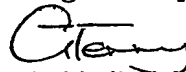
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SMC 60551

APPLICANTS

Avecia Limited

TITLE

COMPOUNDS, COMPOSITIONS AND USES

COMPOUNDS, COMPOSITIONS AND USES

This invention relates to compounds, to compositions containing these compounds, to inks, to printing processes, to printed substrates and to ink-jet printer cartridges.

Ink-jet printing (IJP) is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

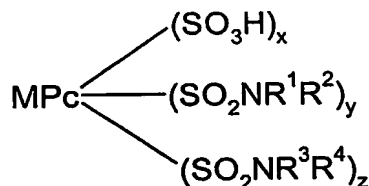
There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water light and ozone fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink-jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate that could block the fine printer nozzles.

Dyes containing a single copper phthalocyanine group and their use in ink-jet printing are known. For example, C.I. Direct Blue 199 and C.I. Direct Blue 86 are used as colorants in commercial ink-jet printing inks. There are also newer phthalocyanines such as those described in US 6,149,722. However, there is a continuing need to provide colorants having superior properties in ink-jet printing inks.

A particular problem for photorealistic quality printing is that of permanence, that is the ability of the colourants used in producing a photographic print to retain their colour properties over a number of years. A key factor contributing to the poor permanence of prints is the quenching of printed colorants by atmospheric pollutants, such as ozone.

We have now found certain cyan colorants suitable for use in ink-jet printing with improved permanence and especially improved ozone-fastness.

According to the present invention there is provided a compound of Formula (1) and salts thereof:



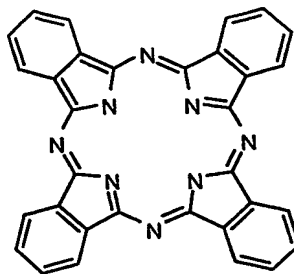
Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of Formula (2);

2



Formula (2)

5 R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;

R^4 is optionally substituted C_{1-4} -hydroxyalkyl;

x is greater than 0 and less than 1.8;

y and z are both greater than 0; and

the sum of $(x+y+z)$ is 2.4 to 4.5.

10 Preferably R^1 , R^2 and R^3 independently are H or methyl, more preferably R^1 , R^2 and R^3 are all H.

R^4 may comprise more than 1 hydroxy group, although preferably R^4 comprises a single hydroxy.

Preferably R^4 is unsubstituted C_{1-4} -hydroxyalkyl, more preferably C_2 -hydroxyalkyl.

15 Preferred optional substituents which may be present on R^1 , R^2 , R^3 and R^4 are independently selected from: optionally substituted alkoxy (preferably C_{1-4} -alkoxy), optionally substituted aryl (preferably phenyl), optionally substituted aryloxy (preferably phenoxy), optionally substituted heterocyclic, polyalkylene oxide (preferably polyethylene oxide or polypropylene oxide), carboxy, phosphato, sulpho, nitro, cyano, halo, ureido, -
20 SO_2F , hydroxy, ester, $-NR^5R^6$, $-COR^5$, $-CONR^5R^6$, $-NHCOR^5$, carboxyester, sulphone, and $-SO_2NR^5R^6$, wherein R^5 and R^6 are each independently H or optionally substituted alkyl (especially C_{1-4} -alkyl). Optional substituents for any of the substituents described for R^1 , R^2 , R^3 and R^4 may be selected from the same list of substituents.

It is especially preferred that R^1 , R^2 and R^3 are all H and R^4 is C_{1-4} -hydroxyalkyl, particularly $-CH_2CH_2OH$.

25 Preferably x is greater than 0 and less than 1.5, more preferably x is greater than 0 and less than 1.2, especially x is greater than 0.05 and less than 1.0 and more especially x is greater than 0.05 and less than 0.5.

Preferably the sum of $y+z$ is in the range of from 2.4 to 4.2, more preferably 2.7 to
30 4.1.

The sum of $(x+y+z)$ is preferably 3.5 to 4.5, more preferably the sum of $(x+y+z)$ is 3.8 to 4.2.

The values for x , y and z in compounds of Formula (1) all represent statistical averages.

Acid or basic groups on the compounds of Formula (1), particularly acid groups, are preferably in the form of a salt. Thus, the Formulae shown herein include the compounds in free acid and in salt form.

5 Preferred salts are alkali metal salts, especially lithium, sodium and potassium, ammonium and substituted ammonium salts (including quaternary amines such as $((\text{CH}_3)_4\text{N}^+)$ and mixtures thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines, more especially sodium salts. The compounds may be converted into a salt using known techniques.

10 The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention.

15 The compounds of Formula (1) have attractive, strong cyan shades and are valuable colorants for use in the preparation of ink-jet printing inks. They benefit from a good balance of solubility, storage stability and fastness to water and light. In particular they display excellent light and ozone fastness. Furthermore they may be prepared from cheap intermediates, avoiding the complexity and expense which is involved in manufacturing some of the more elaborate phthalocyanines.

20 The compounds of Formula (1) may be prepared by condensing copper or nickel phthalocyanine carrying sulphonyl chloride groups and optionally sulphonic acid groups with compounds of formula HNR^1R^2 and HNR^3R^4 wherein R^1 , R^2 , R^3 and R^4 are as hereinbefore defined. The condensation is preferably performed in water at a pH above 7. Typically the condensation is performed at a temperature of 30 to 70°C and the condensation is usually complete in less than 24 hours. The compounds of formula HNR^1R^2 and HNR^3R^4 may be used as a mixture or condensed sequentially with the said
25 phthalocyanine compound.

Copper and nickel phthalocyanines carrying sulphonyl chloride groups and optionally sulphonic acid groups may be prepared by chlorosulphonating copper or nickel phthalocyanine, e.g. using chlorosulphonic acid and optionally a chlorinating agent (e.g. POCl_3 , PCl_5 or thionylchloride).

30 According to a second aspect of the present invention there is provided a composition comprising a compound according to the first aspect of the invention and a liquid medium.

Preferred compositions comprise:

- 35 (a) from 0.01 to 30 parts of a compound according to the first aspect of the invention; and
(b) from 70 to 99.99 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

40 The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates that may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and organic solvent and organic solvent free from water.

When the medium comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₈-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent

may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH_2Cl_2 ; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the compound in the liquid medium. Examples of polar solvents include C_{1-4} -alcohols.

In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C_{1-4} -alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected that gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The liquid media may also contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

Although not usually necessary, further colorants may be added to the composition to modify the shade and performance properties. Examples of such colorants include C.I.Direct Yellow 86, 132, 142 and 173; C.I.Direct Blue 199, and 307; C.I.Food Black 2; C.I.Direct Black 168 and 195; C.I.Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International. Addition of such further dyes can increase overall solubility leading to less kogation (nozzle blockage) for the resultant ink.

Preferably the composition according to the second aspect of the invention is an ink-jet printing ink or a liquid dye concentrate. Concentrates are useful as a means for transporting colorant and so minimising costs associated with drying the dye and transporting excess liquid.

Thus, compositions according to the second aspect of the invention are preferably prepared using high purity ingredients and/or by purifying the composition after it has been prepared. Suitable purification techniques are well known, e.g. ultrafiltration, reverse osmosis, ion exchange and combinations thereof (either before or after they are incorporated in a composition according to the present invention). This purification results in

the removal of substantially all of the inorganic salts and by-products resulting from its synthesis. Such purification assists in the preparation of a low viscosity aqueous solution suitable for use in an ink-jet printer.

Thus, preferably the composition has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C. These low viscosity compositions are particularly well suited for application to substrates by means of ink-jet printers.

Preferably the composition contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a component of the composition).

Preferably the composition has been filtered through a filter having a mean pore size below 10 μ m, more preferably below 3 μ m, especially below 2 μ m, more especially below 1 μ m. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

Preferably the composition contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions.

One embodiment of the invention provides a composition according to the second aspect of the invention which comprises a compound of Formula (1) wherein R¹, R² and R³ are H and R⁴ is -CH₂CH₂OH.

A third aspect of the invention provides a process for forming an image on a substrate comprising applying an composition according to the second aspect of the invention thereto by means of an ink-jet printer.

The ink-jet printer preferably applies the composition to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the ink from the orifice. Alternately the ink can be ejected by an electromechanical actuator connected to a moveable paddle or plunger, for example as described in International Patent Application WO 00/48938 and International Patent Application WO 00/55089.

The substrate is preferably paper, plastic, textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, treated or coated papers which may have an acid, alkaline or neutral character.

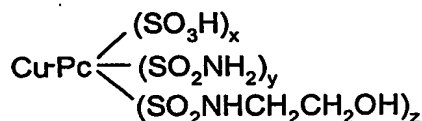
A fourth aspect of the present invention provides paper, plastic, textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or teated papers printed with a composition according to the second aspect of the invention, a compound according to the first aspect of the invention or by means of a process according to third aspect of the invention.

A fifth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in the second aspect of the present invention.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

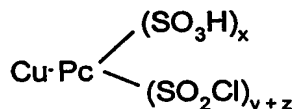
Example 1

Preparation of the following dye wherein x is 0.8 and (y + z) is 3.2:



Stage 1

Preparation of:



Copper phthalocyanine (118.7g; molar ratio 1) was added in portions to a mixture of stirred chlorosulphonic acid (310 ml; molar ratio 23) and phosphorous oxychloride (37.8 ml; molar ratio 2) while keeping the temperature in the range of 50 to 60 °C. The mixture was heated gradually to 140°C, and kept at that temperature, with stirring, for 3 hours. The reaction mixture was then poured onto a mixture of ice (3kg), water (1400ml) and sodium chloride (160g). The precipitate which formed was collected by filtration at reduced pressure and washed with 3% brine (500 ml) before being used in Stage 2.

Stage 2

Preparation of title dye:

Water (2 litre), ethanolamine (24.6 g, molar ratio 2) and 35% ammonia solution (20g; molar ratio 2) were mixed in a 5 litre beaker and then placed in an ice bath (pH = 11.5, temperature 8° C). The phthalocyanine sulphonyl chloride paste (molar ratio 1), resulting from stage 1 above, was slowly added to the mixture while the temperature was kept below 5° C and the pH was maintained at pH 8 by the addition of 10% v/v sodium hydroxide. The reaction mixture was left overnight at room temperature and then heated

at 40°C for 4 hours. Sodium chloride (50% w/v) was added and the resultant precipitate was collected by filtration at reduced pressure and desalinated by dialysis to obtain the title dye wherein x is 0.8 and (y + z) is 3.2.

5 Examples 2 to 9

Example 1 was repeated except that the molar ratios of POCl₃, ethanolamine and ammonia were as shown in Table 1.

10 Examples 10 to 16

Stage 1

 The method of Example 1, stage 1, was repeated except that the molar ratio of POCl₃ used in each example was as shown in Table 1.

Stage 2

 Water (1 litre) and ethanolamine (12g, molar ratio 1) were mixed and then placed in an ice bath. The phthalocyanine sulphonyl chloride pastes (molar ratio 1), prepared as described in stage 1 were slowly added to the mixture while the temperature was kept below 5° C and the pH was maintained at pH 8 by the addition of 10% v/v. ammonia solution. The reaction mixture was left overnight at room temperature and then heated at 40°C for 4 hours. Sodium chloride (20% w/v) was added and the resultant precipitate was collected by filtration at reduced pressure and desalinated by dialysis to obtain the phthalocyanine dyes described in Examples 10 to 16 of Table 1 below.

Table 1

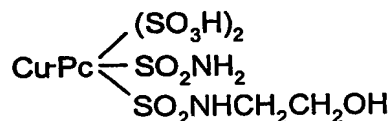
Example	POCl ₃ (molar ratio)	Ethanolamine (molar ratio)	Ammonia (molar ratio)	x	y + z
2	2	4	2	0.1	4.0
3	2	6	2	0.1	4.0
4	2	2	4	1.1	3.0
5	2	2	6	1.0	3.0
6	2.5	2	4	0.4	3.4
7	2.5	4	2	0.2	3.6
8	2.5	2	6	0.2	3.4
9	2.5	2	2	0.6	3.2
10	1.5	1	AR	1.3	2.8
11	2	1	AR	0.8	3.2
12	2.5	1	AR	1.4	2.6
13	3	1	AR	0.8	3.2
14	3.5	1	AR	0.4	3.6
15	3.8	1	AR	0.4	3.8
16	1	1	AR	0.7	3.4

AR – as required to adjust the pH is step (b) to pH 8.0.

5

Comparative Example

The phthalocyanine dye:



10

was prepared as described in Example 1 of US 6,149,722 which preparation is incorporated herein by reference.

15

Examples 17 to 33

Preparation of Inks 1 to 16

The compounds of Examples 1 to 16 (3.5g) were dissolved in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1. In Table 2 below, Ink 1 contains the compound of Example 1, Ink 2 the compound of Example 2 and so on.

20

Preparation of the Comparative Ink

The compound of the Comparative Example (3.5g) was dissolved in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

Example 34Ozone Fastness

The Example Inks 1 to 16 and the Comparative Ink were printed onto a variety of papers using a Canon 5800™ IJ printer. The printed substrate was then assessed for ozone stability using an ozone test cabinet from Hampden Test Equipment. The test was carried out for twenty four hours at 40°C and 50% relative humidity in the presence of 1 part per million of ozone. Fastness of the printed ink to ozone was judged by the difference in the optical density before and after exposure to ozone using a Gretag MacBeth Spectrolino. Thus, the lower the %OD loss the greater the ozone fastness. Results are shown below in Table 2 and these clearly demonstrate that inks based on compounds of this invention display good ozone fastness.

Table 2

Ink	Substrate	% OD loss
Ink 1	HP Premium Plus	2
Ink 1	Canon PR101	48
Ink 1	SEC Premium Photo	53
Ink 2	HP Premium Plus	0
Ink 2	Canon PR101	27
Ink 2	SEC Premium Photo	21
Ink 3	HP Premium Plus	0
Ink 3	Canon PR101	27
Ink 3	SEC Premium Photo	12
Ink 4	HP Premium Plus	2
Ink 4	Canon PR101	53
Ink 4	SEC Premium Photo	54
Ink 5	HP Premium Plus	3
Ink 5	Canon PR101	52
Ink 5	SEC Premium Photo	45
Ink 6	HP Premium Plus	2
Ink 6	Canon PR101	39
Ink 6	SEC Premium Photo	38
Ink 7	HP Premium Plus	3

Ink 7	Canon PR101	30
Ink 7	SEC Premium Photo	28
Ink 8	HP Premium Plus	2
Ink 8	Canon PR101	33
Ink 8	SEC Premium Photo	33
Ink 9	HP Premium Plus	-1
Ink 9	Canon PR101	41
Ink 9	SEC Premium Photo	41
Ink 10	HP Premium Plus	2
Ink 10	Canon PR101	43
Ink 10	SEC Premium Photo	45
Ink 11	HP Premium Plus	1
Ink 11	Canon PR101	37
Ink 11	SEC Premium Photo	39
Ink 12	HP Premium Plus	4
Ink 12	Canon PR101	55
Ink 12	SEC Premium Photo	56
Ink 13	HP Premium Plus	3
Ink 13	Canon PR101	23
Ink 13	SEC Premium Photo	19
Ink 14	HP Premium Plus	0
Ink 14	Canon PR101	17
Ink 14	SEC Premium Photo	12
Ink 15	HP Premium Plus	1
Ink 15	Canon PR101	15
Ink 15	SEC Premium Photo	7
Ink 16	HP Premium Plus	2
Ink 16	Canon PR101	28
Ink 16	SEC Premium Photo	25
Comparative Ink	HP Premium Plus	4
Comparative Ink	Canon PR101	71
Comparative Ink	SEC Premium Photo	64

Further Inks

The inks described in Tables A and B may be prepared using the compounds made in Examples 1 to 16. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

The following abbreviations are used in Table A and B:

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PG = propylene glycol
 DEG = diethylene glycol
 NMP = N-methyl pyrrolidone
 DMK = dimethylketone
 IPA = isopropanol
 MEOH = methanol
 2P = 2-pyrrolidone
 MIBK = methylisobutyl ketone
 P12 = propane-1,2-diol
 BDL = butane-2,3-diol
 CET= cetyl ammonium bromide
 PHO = Na_2HPO_4 and
 TBT = tertiary butanol
 TDG = thiodiglycol

TABLE A

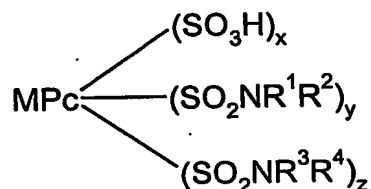
Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2			5	1	
3	10.0	85	3		3	3						1
4	2.1	91		8				0.2	4			5
5	3.1	86	5				0.5				9	
6	1.1	81			9			0.5	6	10	5	4
7	2.5	60	4	15	3	3			10			
8	5	65		20		5				6		5
9	2.4	75	5	4								
10	4.1	80	3	5	2	10		0.3			6	5
11	3.2	65		5	4	6			5	4		
12	5.1	96							5	4		
13	10.8	90	5						1		4	
14	10.0	80	2	6	2	5					15	
15	1.8	80		5							5	
16	2.6	84			11					2		6
14	3.3	80	2			10			3			
15	12.0	90				7	0.3				3	3
14	5.4	69	2	20	2	1					5	
15	6.0	91			4							

TABLE B

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	P12
1	3.0	80	15			0.2				1.2	5	5
2	9.0	90		5		0.15	5.0	0.2		0.12		
3	1.5	85	5	5	4	0.3				0.2		6
4	2.5	90		6								
5	3.1	82	4	8					5			
6	0.9	85		10				0.3				
7	8.0	90		5	5				1		4	11
8	4.0	70		10	4				2		6	
9	2.2	75	4	10	3						3	
10	10.0	91			6		3.0			0.95	5	
11	9.0	76		9	7						6	
12	5.0	78	5	11							7	
13	5.4	86			7					0.1	5	
14	2.1	70	5	5	5	0.1	0.2	0.1	5			
15	2.0	90		10								
16	2	88						10				
14	5	78			5			12			5	
15	8	70	2		8			15			5	
14	10	80						8			12	
15	10	80		10								

CLAIMS

1. A compound of Formula (1) and salts thereof:

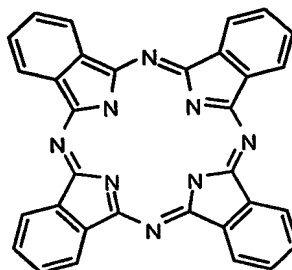


Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of Formula (2);



Formula (2)

R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;
 R^4 is optionally substituted C_{1-4} -hydroxyalkyl;
 x is greater than 0 and less than 1.8;
 y and z are both greater than 0; and
the sum of $(x+y+z)$ is 2.4 to 4.5.

2. A compound according to claim 1 wherein R^1 , R^2 and R^3 are all H.

3. A compound according to either claim 1 or claim 2 wherein R^4 is unsubstituted C_{1-4} -hydroxyalkyl.

4. A compound according to any one of the preceding claims wherein R^4 is C_2 -hydroxyalkyl.

5. A compound according to any one of the preceding claims wherein x is greater than 0 and less than 1.5.

6. A compound according to any one of the preceding claims wherein x is greater than 0 and less than 1.2.

5 7. A compound according to any one of the preceding claims wherein x is greater than 0.05 and less than 1.0.

8. A compound according to any one of the preceding claims wherein x is greater than 0.05 and less than 0.5.

10 9. A compound according to any one of the preceding claims wherein y + z is in the range of from 2.4 to 4.2.

10. A composition comprising a compound as described in any one of claims 1 to 9 and a liquid medium .

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11. A process for forming an image on a substrate comprising applying a composition according to claim 10 thereto by means of an ink-jet printer.

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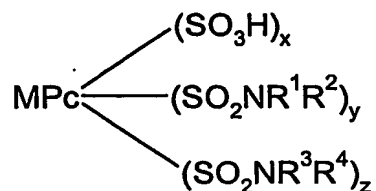
12. A paper, plastic, textile, metal or glass material printed with a composition according to claim 10.

13. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in claim 10.

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ABSTRACT

A compound of Formula (1) and salts thereof:

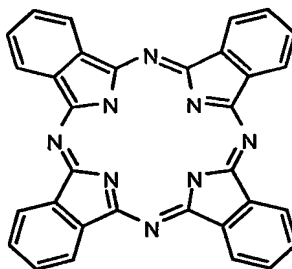


Formula (1)

wherein:

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Formula (2)

R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;

R^4 is optionally substituted C_{1-4} -hydroxyalkyl;

x is greater than 0 and less than 1.8;

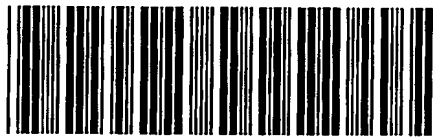
y and z are both greater than 0; and

the sum of (x+y+z) is 2.4 to 4.5.

Also a composition containing a compound of Formula (1), an in-jet printing process, a material printed with a composition a compound of Formula (1) and an ink jet printing cartridge.

PCT Application

GB0304035



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